

Atrazine and Metolachlor in Surface Runoff under Typical Rainfall Conditions in Southern Louisiana

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Atrazine and metolachlor are commonly detected in surface water bodies in southern Louisiana. These herbicides are frequently applied in combination to corn, and atrazine to sugarcane, in this region. A study was conducted on the runoff of atrazine and metolachlor from 0.21 ha plots planted to corn on Commerce silt loam, a Mississippi River alluvial soil. The study, carried out over a three-year period characterized by rainfall close to the 30-year average, provided data on persistence in the surface soil (top 2.5 cm layer) and in the runoff active zone of the soil, as measured by decrease in runoff concentrations with time after application. Regression equations were developed that allow an estimate of the runoff extraction coefficients for each herbicide. Atrazine showed soil half-lives in the range 10.5-17.3 days, and metolachlor exhibited half-lives from 15.8-28.0 days. Concentrations in successive runoff events declined much faster than those in the surface soil layer: Atrazine runoff concentrations decreased over successive runoff events with a half-life from 0.6 to 5.7 days, and metolachlor in runoff was characterized by half-lives of 0.6-6.4 days. That is, half-lives of the two herbicides in the runoff-active zone were one-tenth to one-half as long as the respective half-lives in the surface soil layer. Within years, the half-lives of these herbicides in the runoff active zone varied from two-thirds longer for metolachlor in 1996 to one-fifth longer for atrazine in 1995. The equations relating runoff concentrations of atrazine and metolachlor to soil concentrations contain extraction coefficients of 0.009. Losses in runoff for atrazine were 5.2-10.8% of applied, and for metolachlor they were 3.7-8.0%; atrazine losses in runoff were 20-40% higher than those for metolachlor. These relatively high percent of application losses indicate the importance of practices that reduce runoff of these chemicals from alluvial soils of southern Louisiana.

KEYWORDS: Atrazine; metolachlor; herbicide; runoff; corn; Mississippi River alluvial soil; runoff available residue

INTRODUCTION

When a pesticide is applied to the soil surface, the initial concentration at the surface immediately begins to diminish due to microbial and chemical (including photochemical) degradation and to volatilization (1, 2). Rainfall causes further dissipation from the soil surface through both runoff and leaching processes (1, 3, 4).

Soil pesticide residues that are picked up in a runoff event come from a soil layer possibly as thin as 2-3 mm (5, 6). This location of "runoff available residue" (7) has been referred to as the "mixing zone" (8, cited in ref 7), the "zone of interaction" (5), and the "effective depth of interaction" (9). Below this zone of interaction, the efficiency of mixing of runoff water with the soil decreases (6).

Concentrations of mobile pesticides in runoff are at their highest in the first runoff event after application. Following this event, concentrations in runoff steadily decrease in subsequent runoff, as is also observed throughout a single runoff occurrence (7, 10). In a number of studies over the past 25 years, concentrations of commonly used herbicides in runoff have been shown to drop rapidly (**Table 1**). Rates of decrease, expressed as $t_{1/2}$, have varied from 1 to 27 days for atrazine, 3–17 days for metolachlor, and intermediate values for metribuzin and alachlor. Interestingly, half-lives of the herbicides in the surface soil, when they are reported along with runoff concentrations, are 2–4 times as long (**Table 1**). This difference is reasonably the difference between the rapid drop in herbicide concentration in the top few millimeters of soil, measured by runoff concentration, and the slower dissipation in concentration in the zone that is sampled for soil residues (7, 11).

Leonard et al. (12) (see also ref 7) developed an equation relating concentrations of water-transported herbicides (a series of triazines and a phenylbenzeneacetamide) in soil to runoff concentrations, obtaining $r^2 = 0.86$. In this equation

$$Y = 0.05X^{1.2} \tag{1}$$

X is the herbicide concentration in the top 1 cm of soil at the

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Table 1. Half-Life Values of Herbicides in Runoff and Soil

| | half-life, days | | | |
|-------------|-----------------|------|--------|--|
| herbicide | runoff | soil | ref | |
| atrazine | 7 | | 30, 31 | |
| | 2.2 | _ | 28 | |
| | 0.9 | _ | 28 | |
| | 2-3 | 6 | 12 | |
| | 3-27 | | 32 | |
| | 8.7 | 34.6 | 16, 20 | |
| | 3.6 | _ | 29 | |
| | 5.7 | _ | 33 | |
| metribuzin | 5 | _ | 32 | |
| | 2.6 | _ | 33 | |
| alachlor | 3.1 | _ | 33 | |
| metolachlor | 17.3 | 34.7 | 26 | |
| | 8.4 | 23.1 | 16, 20 | |
| | 3.2 | _ | 29 | |
| | 13.3 | 21.8 | 34 | |

time of the runoff event, and Y is the concentration in runoff. The coefficient 0.05 was termed an extraction coefficient, representing removal of pesticide residues in the top 1 cm soil layer into runoff. Data for atrazine, cyanazine, propazine, and diphenamid went into the equation. The nonlinearity of the relationship, reflected by the exponent, may indicate that the runoff extraction efficiency was greater early in the runoff season and decreased as time after application increased. Another possibility suggested by these workers was that as the season progressed, the actual surface concentration exposed to runoff may have been overestimated. Leonard and Wauchope (13) observed that the extraction coefficient normally lies in the range 0.05-0.2. They suggested that 0.1 was a good estimate in most cases.

Since 1992 the Louisiana Department of Agriculture and Forestry has been sampling surface water bodies throughout the state for various agricultural chemicals. Atrazine is the most frequently detected herbicide in lakes, bayous, and streams of southern Louisiana; metolachlor is also commonly observed in this sampling program. These water quality data for southern Louisiana have been summarized by Southwick et al. (14). These two chemicals are often applied together to corn, and atrazine is commonly applied to sugarcane.

We report here results from a three-year, four-replicate study of the runoff of atrazine and metolachlor from plots cultivated to corn on a Mississippi River alluvial soil. As did Leonard, Wauchope, and colleagues, we relate runoff concentrations of atrazine and metolachlor to their soil concentrations and develop extraction coefficients for each herbicide. After the papers of Leonard et al. (12) and of Leonard and Wauchope (13), few reports have presented a detailed analysis of the relationship between runoff concentrations and soil concentrations. A preliminary paper on the 1995 runoff results, not containing the analysis of the soil-runoff concentration relationship, has been made (15). We have reported runoff of atrazine and metolachlor from corn cultivation in a one-year study from plots

with and without subsurface drains (16, 17). This earlier work was discontinued when the plots were converted to soybean in 1988. We are unaware of other reports of atrazine and metolachlor in runoff from corn in Mississippi River alluvial soils of Louisiana. Selim (18) has reported runoff of atrazine from these soils in sugarcane cultivation.

MATERIALS AND METHODS

The field work was conducted on plots at Louisiana State University's Ben Hur Farms (6 km south of Baton Rouge in East Baton Rouge Parish). The plots were on Mississippi River alluvial soil [Commerce loam grading to silt loam (fine-silty, mixed, nonacid, thermic, Aeric Fluvaquents); Ap horizon: 20.0% clay, 39.6% silt, 40.4% sand, 0.43% OM] and planted to corn. Willis et al. (19) describe in detail the plot design, which was installed to test influences of subsurface drainage and water table control on runoff losses of agricultural chemicals. In short, plots 35×61 m (0.21 ha) were laid out on a 0.2% slope. The study plots in the present work were the four of a 16-plot randomized complete block design not containing subsurface drains. The plots contained borders 15 cm high to direct the runoff through H-flumes. Aliquots (50 mL from every 1000 L of flow) were collected by automatic samplers (800SL Refrigerated Sampler with an integral flowmeter, American Sigma, Loveland, CO) that kept the samples at 5 °C until they could be removed to the laboratory, usually within 1 day of each runoff event. Soil samples from the top 2.5 cm layer were collected periodically. Planting and application information are listed in Table 2.

Soil samples were collected three times in the first two weeks and 3-4 additional times within the following 5-6 months after application. Soil was sampled by scooping all material from a 10-cm diameter aluminum ring that was 2.5 cm deep; 10 ring samples were collected from each plot and combined to make a composite. Preapplication samples were also collected. During the 1980s the land was grown to corn with atrazine and/or metolachlor applications. Soils were allowed to air-dry in the laboratory (the wettest soils required up to 7 days to dry), ground in a Wiley mill (Standard Model No. 3 from Arthur H. Thomas Co., Philadelphia, PA) to pass a 2 mm sieve, and then frozen at -5 °C until analysis. Runoff samples (50 mL aliquots from each 1000 L of runoff) were automatically collected in 1 L wedge-shaped plastic bottles during runoff events. If more than one bottle contained sample from a runoff event, flow-weighted aliquots were removed from each bottle to make a composite. Runoff samples were also frozen until analysis. Soils (20 g aliquots) were extracted by Soxhlet with 200 mL of ethyl acetate for 24 h, and the extract was dried by filtering through sodium sulfate. Recoveries from spiked soil that was spread out on a tray for 7 days were 95% \pm 6% for atrazine, and 85% \pm 9% for metolachlor (n = 4). Runoff samples (250 mL, including sediment) were stirred for 4 h with 100 mL ethyl acetate; the extract was dried in the same manner as soil extracts. Recoveries from runoff samples (determined with water samples containing 5000 mg/L of spiked soil) were 112% \pm 7.7% for atrazine and 82.7% \pm 12.9% for metolachlor (n = 4). Analytical results were not corrected for recoveries. Extracts were analyzed by gas chromatography (Tracor 540 Gas Chromatograph, Tracor Instruments, Austin, TX) with electron capture detection. The injector port was held at 240 °C and the detector at 360 °C; helium carrier gas flow was 3 cm³/min, and nitrogen makeup flow was 50 cm³/min. For atrazine, a 30 m DB5 column (0.53 mm id, 5 μ m film

Table 2. Planting and Application Data

| corn | | herbicide | herbicide rates, ^a | | estimated initial soil conc., top 2.5 cm, ng/g ^b | |
|----------|----------|-------------|-------------------------------|-------------|---|-------------|
| planting | | application | kg/ha | | | |
| season | date | date | atrazine | metolachlor | atrazine | metolachlor |
| 1995 | April 20 | April 27 | 0.75 | 0.95 | 2100 | 2600 |
| 1996 | March 29 | March 29 | 1.49 | 1.91 | 4000 | 5100 |
| 1997 | April 22 | April 24 | 1.49 | 1.91 | 4000 | 5100 |

^a Herbicides were applied by tractor as Bicep 6L (1995), Bicep (1996), and Bicep II (1997), all in a volume of 140 L/ha. The application was not incorporated, and conventional tillage was followed. ^b This calculation assumes that the top 15 cm layer weighs 0.9×10^6 kg.

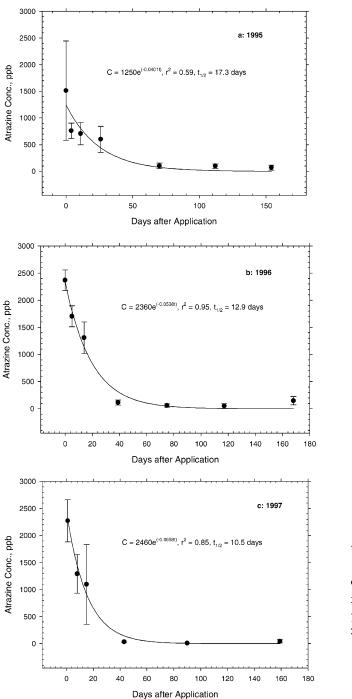


Figure 1. Atrazine concentration in soil, 1995–1997.

thickness) was used at 210 °C; for metolachlor, a 30 m DB210 column (0.53 mm id, 1 μ m film thickness) was used at 165 °C. In the gas chromatographic analyses, external standards of the two herbicides were used to develop calibration curves. Limits of detection (based on both spiked and preapplication samples) in runoff were 3 μ g/L for atrazine and 2 μ g/L for metolachlor (250 mL sample); from soil, limits of detection were 25 ng/g for both atrazine and metolachlor (20 g sample). Only single samples of soil and runoff were analyzed, and a surrogate compound was not added to the samples.

Regression equations were developed with TableCurve 2D v. 4 (Jandel Scientific, San Rafael, CA) and with SAS v. 8 (SAS Institute, Inc., Cary, NC).

RESULTS AND DISCUSSION

The concentration of atrazine (**Figure 1**) and metolachlor (**Figure 2**) in the top 2.5 cm soil layer in each of the study

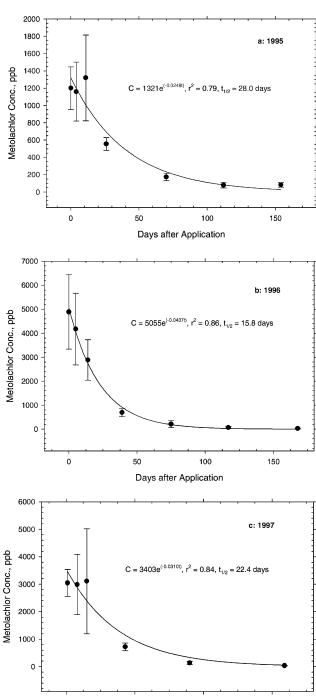


Figure 2. Metolachlor concentration in soil, 1995–1997.

0

years showed the expected rapid decay. First-order regression equations have been fit to the data in **Figures 1** and **2**. Over the three-year period, atrazine soil half-lives ranged from 10.5 to 17.3 days, and those for metolachlor ranged from 15.8 to 28.0 days. Metolachlor's half-life, in each year greater than that for atrazine, was slightly higher in 1996 to more than double in 1997, but none of these persistence differences within years between the two herbicides was significant (P = 0.10). In contrast to these results, in an earlier study Southwick et al. (20) measured for the surface (2.5 cm) soil layer a two-thirds longer half-life for atrazine (35–36 days) rather than metolachlor (20–23 days). We do not have an explanation for the reversal in relative half-lives between the two herbicides in these two studies. Hornsby et al. (21) reported wide ranges for field half-

100

Days after Application

150

Table 3. Rainfall, Runoff, and Runoff/Rainfall Ratios

| day | rain, mm | runoff, mm ^a | runoff/rair |
|---------|----------|-------------------------|-------------|
| | | 1995 | |
| 11 | 72.6 | 53.5 | 0.74 |
| 13 | 16.8 | 3.7 | 0.22 |
| 21 | 36.8 | 4.6 | 0.12 |
| 33 | 39.1 | 6.2 | 0.16 |
| 37–66 | 88.1 | 0.6 | 0.01 |
| total | 253.4 | 68.6 | 0.27 |
| | | 1996 | |
| 1 | 52.1 | 41.4 | 0.79 |
| 8 | 23.9 | 7.2 | 0.30 |
| 15 | 78.7 | 76.2 | 0.97 |
| 16 | 35.1 | 26.4 | 0.75 |
| 25 | 31.2 | 21.3 | 0.66 |
| 31 | 20.6 | 17.8 | 0.86 |
| 40 | 60.7 | 52.6 | 0.87 |
| 41–109 | 256.8 | 7.5 | 0.029 |
| total | 579.7 | 250.4 | 0.43 |
| | | 1997 | |
| 2 | 54.0 | 11.9 | 0.22 |
| | 68.8 | 68.8 | 1.00 |
| 9 | 23.2 | 23.2 | 1.00 |
| 27-28 | 22.6 | 4.2 | 0.19 |
| 30 | 50.6 | 50.6 | 1.00 |
| 34-37 | 83.4 | 65.5 | 0.79 |
| 43 | 57.2 | 36.3 | 0.63 |
| 54 | 195.8 | 77.8 | 0.40 |
| 56-63 | 52.1 | 18.2 | 0.35 |
| 64-98 | 121.0 | 2.5 | 0.02 |
| 99 | 54.9 | 39.0 | 0.71 |
| 102-106 | 31.5 | 2.0 | 0.06 |
| total | 815.1 | 400.0 | 0.49 |

 $^{^{}a}$ 1 mm = 2100 L from a 0.21 ha plot.

lives for atrazine and metolachlor; they estimated initial (immediately after application) values of 60 days for atrazine and 90 days for metolachlor.

Rainfall and runoff for the three seasons are listed in **Table 3**. The 30-year average rainfall for the area is 1500 mm. Rainfalls for 1995 (1690 mm), 1996 (1590 mm), and 1997 (1860 mm) were 6–24% greater than the average. The several occasions in 1996 and 1997 when runoff/rainfall ratios were >0.8 are due to the low hydraulic conductivity of the plow layer of the soil: 1 mm/h (22). Surface sealing quickly occurs, and in heavy rainfall, a high percentage of rainfall leaves the field in runoff.

Concentrations of atrazine (**Figure 3**) reached highs of 100— 410 μ g/L in the first runoff events of the seasons. The lowest first-event concentrations (50–100 μ g/L) occurred in 1995, when the application rate was lower (one-half of the 1996 and 1997 rates; Table 2) and when the first runoff event was latest (day 11 for 1995). In the succeeding seasons, the first events occurred on day 1 (1996) and day 2 (1997) and produced concentrations of 140-410 μ g/L (1996) and 160-270 μ g/L (1997). Metolachlor concentrations (Figure 4) in the first runoff of the seasons were in the range $70-360 \mu g/L$. As for atrazine, the lowest first-event metolachlor concentrations (50–70 μ g/ L) occurred in 1995, again in line with the lower application rate in that year (Table 2) and the later time for the first event. In 1996 the day 1 concentrations were $160-360 \mu g/L$, and in 1997 the day 2 concentrations were 150-190 μ g/L. For each season, the mean atrazine concentration was higher than that for metolachlor in the first runoff event, in contrast to both the 20% lower application rate (Table 2) and the lower water solubility of atrazine (33 mg/L, compared to metolachlor, 530 mg/L) but consistent with the lower K_{oc} for the former (100 mL/g) compared to the latter (200 mL/g), as listed in the

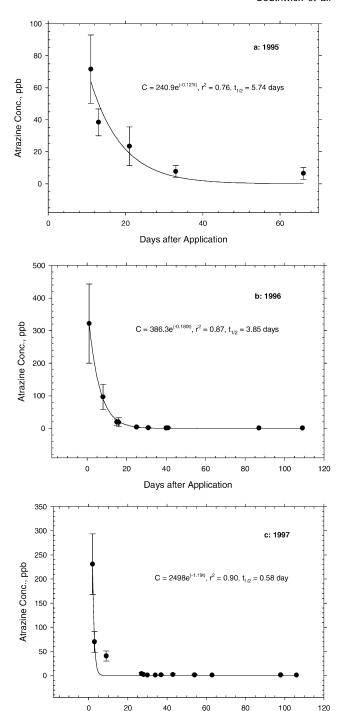


Figure 3. Atrazine concentration in runoff, 1995–1997.

tabulation of Hornsby et al. (21). Selim and co-workers have measured K_{oc} 's for atrazine (160 mL/g; 18, 23) and metolachlor (192 mL/g; 23] on Commerce silt loam. Even though these first runoff event concentration differences between atrazine and metolachlor were consistently observed, the differences were not significant (Microsoft Excel paired t-test, $P \ge 0.16$). In an earlier study (1987) of runoff of these herbicides from corn cultivation (16), twice the application rate of 1995 led to first event (day 12) concentrations that were higher than the 1995 day 11 concentrations of atrazine and metolachlor and were comparable to first event concentrations of 1996 and 1997. The application rate for 1987 was similar to that for 1996 and 1997, and the runoff-available residue 12 days after application in 1987 was similar to the runoff-available residues on day 1 in 1996

Days after Application

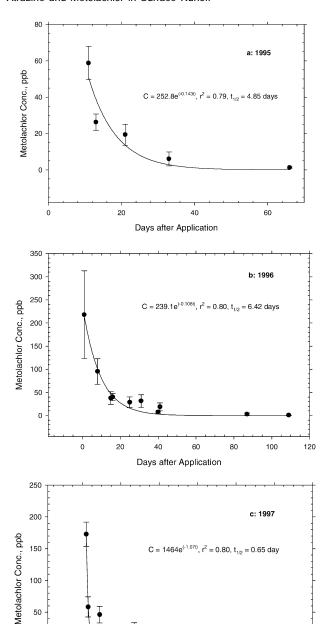


Figure 4. Metolachlor concentration in runoff, 1995–1997.

20

0

and on day 2 in 1997. Surface soil concentrations immediately after application were similar in 1987 (20), 1996, and 1997.

40

60

Days after Application

80

100

120

Runoff concentrations of pesticides over time (**Figures 3** and **4**) show the decrease in runoff-extractable residues as time increases after application. The behavior of the runoff concentrations of atrazine and metolachlor in our 1995 and 1996 studies fits first-order regression equations with coefficients of determination ≥ 0.76 (**Figures 3a,b** and **4a,b**) and allows calculation of the half-lives of these extractable soil residues. Because of large rainfall early in the 1997 season (129 mm of rain in four days, **Table 4**), runoff concentrations dropped extremely rapidly. For 1997 the first-order equations ($r^2 \geq 0.80$) developed by TableCurve and by SAS yielded C_0 values for atrazine and metolachlor that were severalfold greater than those observed in 1995 and 1996 (**Figures 3c** and **4c**). Higher runoff concentrations of mobile herbicides have been observed in studies with

Table 4. Herbicide Concentrations and Losses in Runoff

| | | atrazine | | metolachlor | |
|------------------------------|-----------------|----------------|-----------------|----------------|----------------|
| | runoff, | concentration, | loss, | concentration, | loss, |
| day | mm ^a | μ g/L | g/ha | μ g/L | g/ha |
| | | 1995 | | | |
| 11 13 | 53.5 3.7 | 66.8 38.1 | 35.7 1.4 | 60.8 26.2 | 32.5 1.0 |
| 21 | 4.6 | 25.2 | 1.2 | 19.3 | 0.9 |
| 33 66 | 6.2 0.2 | 6.2 6.6 | 0.4 0.01 | 6.1 1.3 | 0.4 0.003 |
| total loss | | | 38.7 | | 34.8 |
| (% of applied) | | | (5.2) | | (3.7) |
| | | 1996 | | | |
| 1 8 | 41.4 7.2 | 321.8 96.6 | 133.2 7.0 | 217.8 95.2 | 90.2 6.9 |
| 15 | 76.2 | 18.9 | 14.4 | 37.8 | 28.8 |
| 16 25 | 26.4 21.3 | 18.5 4.0 | 4.9 0.8 | 40.2 28.6 | 10.6 6.1 |
| 31 | 21.3 17.8 | 4.0 1.8 | 0.8 | 28.6 31.4 | 5.6 |
| 40 | 52.6 | 1.0 | 0.5 | 7.5 | 3.9 |
| 41–109 | 7.5 | 1.1 | 0.1 | 7.8 | 0.6 |
| total loss (% of applied) | | | 161.2 (10.8) | | 152.7 (8.0) |
| (70 of applica) | | 1997 | ` ' | | (0.0) |
| 2 | 11.9 | 230.8 | 27.5 | 172.8 | 20.6 |
| 3 | 68.8 23.2 | 69.8 40.5 | 48.0 9.4 | 58.5 46.1 | 40.2 10.7 |
| 9 27–28 | 4.2 | 40.5 2.7 | 9.4 0.1 | 16.6 | 0.7 |
| 30 | 50.6 | 1.0 | 0.4 | 18.8 | 7.3 |
| 34–37 43 | 65.5 36.3 | 1.2 2.0 | 0.8 0.7 | 13.5 7.1 | 8.8 2.6 |
| 54 | 77.8 | 1.2 | 0.9 | 2.6 | 2.0 |
| 63 99 | 18.2 39.0 | 1.0 1.1 | 0.2 0.4 | 2.7 1.1 | 0.5 0.4 |
| 106 | 2.0 | 1.0 | 0.02 | 1.8 | 0.04 |
| total loss (% of applied) | | | 88.4 (6.0) | | 93.8 (5.0) |
| (70 or applied) | | | (0.0) | | (3.0) |

 $^{^{}a}$ 1 mm = 2100 L.

simulated rainfall applied soon after application. Edwards et al. (24) measured concentrations of atrazine and alachlor in the $2000-7000~\mu g/L$ range in pools formed in surface depressions in a corn field when simulated rainfall was applied on days 1, 2, 4, and 8 after application of the herbicides. Abdel-Rahman et al. (25), with tilted beds of packed soil, measured in splash/runoff from simulated rain concentrations of atrazine in excess of $70~000~\mu g/L$ and of alachlor exceeding $20~000~\mu g/L$. These investigators concluded that an atrazine concentration in runoff twice its water solubility indicated the transfer of particulate material in the splash/runoff event. Within-year comparisons between the equations for atrazine and metolachlor reveal significant differences for 1996 (**Figures 3b** and **4b**) between both the C_0 's (P < 0.01) and the k's (P = 0.01) (SAS).

The half-lives of runoff extractable residues (**Figures 3** and **4**) are shorter than the half-lives of the respective soil residues (**Figures 1** and **2**). Residue half-lives in the surface soil layer ranged from 10.5 to 17.3 days for atrazine (**Figure 1**) and from 15.8 to 28.0 days for metolachlor (**Figure 2**). Half-lives for the concentrations in runoff ranged from 0.58 to 5.74 days for atrazine (**Figure 3**) and from 0.65 to 6.42 for metolachlor (**Figure 4**). Half-lives of the residues in the runoff extraction zone of the soil was 0.09–0.33 of that in the surface soil for atrazine and 0.04–0.41 for metolachlor. This difference may be due to leaching of these runoff available residues to below the runoff extraction zone, but other surface processes such as volatilization, photolysis, and microbial degradation may be significant too (7, 1). Another explanation for the observation of decreasing concentrations in runoff over time may be rapid

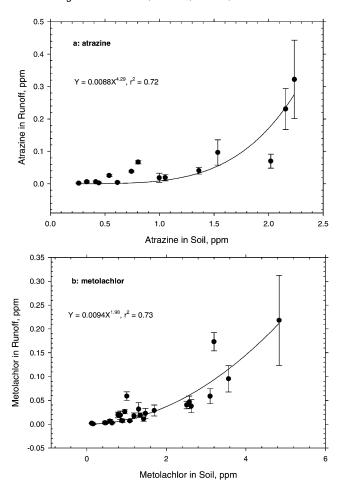


Figure 5. (a) Atrazine concentration in runoff/concentration in soil and (b) metolachlor concentration in runoff/concentration in soil.

desorption from sites of lower binding energies followed by slower desorption from sites of higher binding energies (26).

As in the work of Leonard et al. (12), the soil data of **Figures 1** and **2** and the runoff data of **Figures 3** and **4** can be combined to produce **Figure 5** and to develop equations, similar to eq 1, relating runoff concentrations to soil concentrations for the herbicides. Equation 2 relates the 1995–1997 data for atrazine, and eq 3 is the metolachlor regression:

$$C_{\text{runoff}} = 0.0088(C_{\text{soil}})^{4.29}, \qquad r^2 = 0.72$$
 (2)

$$C_{\text{runoff}} = 0.0094(C_{\text{soil}})^{1.98}, \qquad r^2 = 0.73$$
 (3)

The extraction coefficient < 0.010 and the exponent \geq 2.0 reflect the rapid drop in herbicide concentration in the runoff extraction zone, compared to the concentration in the soil sampling section of the surface 2.5 cm. The runoff/soil concentration ratio is high in the first runoff event; this ratio quickly drops in subsequent events. We reported similar equations in an earlier study (16) of runoff of atrazine, eq 4, and metolachlor, eq 5:

$$C_{\text{runoff}} = 0.034(C_{\text{soil}})^{1.9}, \qquad r^2 = 0.69$$
 (4)

$$C_{\text{runoff}} = 0.013(C_{\text{soil}})^{1.4}, \qquad r^2 = 0.73$$
 (5)

Percent of application losses (**Table 4**) varied from 5.2% to 10.8% for atrazine and from 3.7% to 8.0% for metolachlor. As is frequently the case, the first one or two runoff events accounted for most of the runoff. For atrazine, 84–96% of the

season's losses occurred within the first two events, and 63-96% of metolachlor's runoff was accounted for within the first two events. But only in 1995 did most of the runoff water volume occur in the first two events. In that year 84% of the runoff occurred on days 11 and 13. In 1996, only 19% of the runoff occurred on the first two runoff days, and in 1997 18% came off the field on these 2 days. The same reason that causes runoff concentration decrease (diminishing residue concentrations in the runoff active zone) also leads to a decrease in total runoff losses/event as runoff events accumulate. Selim (18) reports 2-11% application losses of atrazine in runoff from Commerce silt loam in sugarcane cultivation. These percent of application losses reported by us from corn and by Selim from sugarcane are 2-3 times as great as those reported for atrazine by Wauchope (27) in his review of field research in various areas of the US.

In these studies, percent of application losses of atrazine in runoff were 20% (1997) to 40% (1996) greater than metolachlor in runoff, even though metolachlor's application rate was 28% higher (**Table 2**). This trend is in line with the K_{oc} values for these two chemicals on Commerce soil (18, 23). In our earlier work with these two herbicides, percent of application losses for atrazine was essentially the same as that for metolachlor (16). Triplett et al. (28) reported slightly greater losses of simazine compared to atrazine, even though the K_{oc} for simazine [130 mL/g (21)] is greater than atrazine's. Gaynor et al. (29) reported that over a period of four application seasons, runoff of atrazine was greater than that of metolachlor for two of the seasons, the same once, and less once; in all seasons, the metolachlor application rate was greater than that for atrazine. Our earlier experience with these herbicides and the observations of Gaynor suggest that the consistent trends with respect to K_{oc} 's in our present work was fortuitous. This variability in percent of application losses is an indication of the complicated interplay among the various dissipation routes after application.

In summary, atrazine and metolachlor in this three-year study showed half-lives in the surface layer of soil (top 2.5 cm layer) of less than 30 days. The half-lives measured for metolachlor were greater than those for atrazine, and in one season metolachlor's half-life was over twice as long as atrazine. For these herbicides, persistence in the runoff active zone of the soil, as measured by the half-lives of the runoff concentrations, was 0.09-0.41 as long as persistence in the 2.5 cm surface layer. The two lowest values (0.14 for atrazine and 0.09 for metolachlor) occurred in 1997, the season of greatest rainfall. The equations relating runoff concentrations of atrazine and metolachlor to soil concentrations contained extraction coefficients 0.009 and exponents of 2.0 (metolachlor) and 4.3 (atrazine). These low extraction coefficients and exponents considerably larger than 1.0 reflect the high herbicide concentrations in the top few mm layer of soil (applications were not incorporated) that produce high concentrations in initial runoff but that quickly drop with rainfall and runoff to produce correspondingly low concentrations in subsequent runoff events. Relative half-lives of the herbicides in the runoff active zone varied: in 1996 that for metolachlor was two-thirds greater than that for atrazine; in 1995 atrazine's half-life in the runoff active zone was one-fifth longer. Runoff in relation to rainfall was high, and consequently percent of application losses of the herbicides was high. Even when rainfall did not occur until the second week after application in 1995, atrazine in runoff was 5.2% and metolachlor in runoff was 3.7% of application. These relatively high losses in runoff from these soils in this climate indicate the value of runoff reducing practices in agricultural fields for water quality concerns in southern Louisiana. In the absence of deep-chiseling,

subsurface drains do not reliably reduce runoff from these soils (B. C. Grigg, L. M. Southwick, J. L. Fouss, anad T. S. Kornecki. Drainage system impacts on surface runoff, nitrate loss and crop yield on a southern alluvial soil. Submitted to *Trans. ASAE*).

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